MESOSCOPIC DYNAMICS OF SOLID-LIQUID INTERFACES. A GENERAL MATHEMATICAL MODEL

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ABSTRACT. A number of chemical and physical processes occur at interfaces where solids meet liquids. Among them is heap and in-situ leaching, an important technological process to extract uranium, precious metals, nickel, copper and other compound. To understand the main peculiarities of these processes a general mathematical approach is developed and applied. Its key point is new conditions at the free (unknown) boundary between liquid and solid phases (pore space-solid skeleton). The developed model can be used to analyze the dependence of the dynamics of the free fluid-skeleton interface on the external parameters of the process, like temperature, pressure, reagent concentration and others. Therefore, the overall behavior of the process can be controlled either by the rate of chemical reaction on the free interface via reagent concentration or by the velocity at which dissolved substances are transported to or from the free surface.

The special attention is paid to a plausible justification of upscaling from mesoscopic to macroscopic scales and its comparison with approaches usually used at the moment. Several examples illustrate the feasibility of the models.

Keywords: solid-liquid interface, leaching, fluid flow.

1. INTRODUCTION

Ability to control chemical and physical processes at interfaces is important to control a variety of technological processes, in particular heap and in-situ leaching.

For this purpose it should be possible to perform numerical simulation and analysis of the processes under consideration. So far these processes are described at the macroscopic scale by the variety of mathematical models (see [1], [2], [3], [4], and references there in). As a rule, people deal with so called phenomenological two phase models when at each point of a continuous medium there are both the solid skeleton and the liquid. All these models are based on the same principles:

- Fluid dynamics is described by Darcy's system of filtration or some its modification;
- The migration of active compound and products of chemical reactions are described by somehow postulated convection-diffusion equations for the appropriate concentrations.

The main thing in these postulates is the form and coefficients of differential equations. There is a variety of approaches how to choose in dependence of the tastes and preferences of the authors. It is quite explainable because the basic mechanism of the physical process on the macroscale is formed on microscale of the unknown (free) boundary between the pore space and the solid skeleton. But exactly this basic mechanism is not used in the models! Really, dissolution of rocks takes place exactly there, the concentration of the injected reagent and the geometry of the pores are changed on this interface as well. Moreover, the flow of the products of chemical reactions inward the pore space is generated on this scale also. But at the same time, all of the aforementioned standard macroscopic mathematical models operate with other, much larger, scales and hence just do not "see" neither free boundary nor peculiarities of the interaction of the reagent and skeleton on this boundary. This explains such a variety of macroscopic mathematical models.

R. Burridge and J. B. Keller [5] and E. Sanchez-Palencia [6] were the first who explicitly stated that mathematical models to describe multiscale processes must be rigorously derived from micro- to macroscale by the following successive steps:

(a) to develop a mathematical model describing the physical process at the microscopic level with maximal accuracy (exact model);

(b) to distinguish a set of small parameters characterizing difference in scales of the model;

(c) to derive the macroscopic model as the asymptotic limit of the exact model. Various particular implementations of this approach are analysed in [7], [8].

The most systematic implementation of this scheme have been studied by A. Meirmanov [8] – [12] on the base of dimensionless forms of the mathematical models. In this way it becomes possible to simplify microscopic mathematical models and to find exact asymptotic approximations, adequately describing physical processes at the macroscopic level.

In what follows we implement the stages (a)-(c) on the theoretical level. To do that we use the above mentioned Meirmanov's approaches and models [8] together with methods, developed for the free boundary problems [13].

The paper deals with a dissolution of a solid porous skeleton by an active admixture (acid) dissolved in an inviscid incompressible pore liquid. As a result of a dissolution of the solid skeleton appear products of chemical reactions. The process is considered in a bounded domain $\Omega \subset \mathbb{R}^3$ with boundary S. Next, let us consider $S^+ \subset S$ as a set of injection wells, $S^- \subset S$ is considered as production wells, while $S^0 \subset S$ represents impermeable insoluble piece of the boundary.
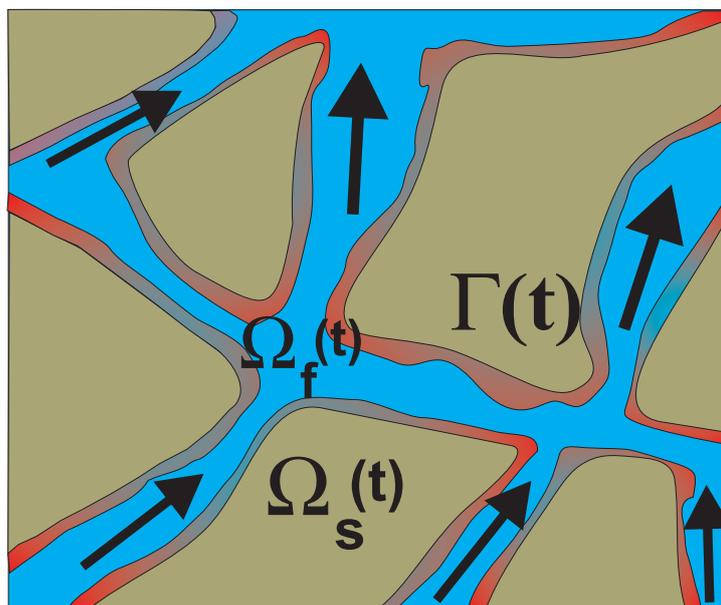
Fig. 1. The pore space.

In order to introduce the microscale level of the process, the domain Ω is treated as consisting of the pore space $\Omega_f(t)$, and the solid skeleton $\Omega_s(t)$. The dissolution process takes place at the interface $\Gamma(t)$ between the pore space and solid skeleton (see Fig. 1). It is worth mentioning that $\Gamma(t)$ is a free (unknown) surface, because during the leaching the skeleton is dissolved and changes its shape. These mathematical problems are called *free boundary problems.*

The mathematical model of leaching at the microscale is based on classical equations of continuum mechanics and some trustworthy relations characterizing well-known chemical reactions [14]. To complete the model we need to derive a new boundary conditions, describing dissolution of the solid skeleton at the free boundary and dynamics of the boundary itself. The next step is the proper description of the process at the macroscale, known as upscaling or homogenization. To perform this step correctly we need very new developments in mathematics dealing with "two-scale convergence"([8],[9]).

Let us begin with some general remarks to describe the steps doing to derive the mathematical model of the leaching at the microscale. For the first of all, fluid flow in pores at the microscopic level is very slow (a few meters per year) therefore the convection terms in Navier-Stokes equations can be neglected, hence Stokes equations for incompressible viscous liquids are good approximation. The correct mathematical model of propagation of active admixtures in pore space (microscopic level) should take into account the both convection and diffusion. Really, without diffusion the reverse flow of the reaction products from the free surface $\Gamma(t)$ inward the pore space blocks the flow of the reagent and finally cancels chemical reaction. Thus, the diffusion – convection equation must be used to describe propagation of the active reagent (acid).

For the concentrations of the products of chemical reactions we use the transport equations without diffusion terms. This equation is of the first order in space and needs boundary condition only on the parts of the boundary $\partial\Omega_f(t)$ where the liquid starts the motion inward the pore space, that is at the free boundary $\Gamma(t)$ and injection wells S_i^+.

Looking ahead let us note, that a diffusion process in the liquid is also very slow, therefore to balance the process some oscillations should happen, at least at the initial stage. Really, the rate of outflow of fluid from the free boundary is proportional to the concentration of the acid and grows when this concentration increases. The domination of outflow of fluid from the free boundary makes less the diffusion of the reagent and leads to decreasing of its concentration at the free boundary. In turn, it implies the decreasing of the outflow of fluid from the free boundary and the domination of the diffusion of the acid to the free boundary. The growth of the diffusion of the reagent to the free boundary leads to the growth of its concentration at the free boundary and so on.

2. MATHEMATICAL MODEL OF THE LEACHING FOR MICROSCOPIC MODEL

2.1. Statement of the initial-boundary value problem for the microscopic level.

Let us introduce characteristic length L and time T. In dimensionless variables

$$\boldsymbol{x} \to \frac{\boldsymbol{x}}{L}, \ t \to \frac{t}{T}, \ \boldsymbol{v} \to \frac{T}{L}\,\boldsymbol{v}, \ p \to p^* \, p,$$

the dynamics of liquid in pore space $\Omega_f(t)$ is described by Stokes equation

$$(1) \qquad\qquad \alpha_\mu \triangle \boldsymbol{v} - \nabla p = 0,$$

for the pressure p and velocity $\boldsymbol{v}$.

The continuity equation is used in its generalized form [15], that is as a continuity equation for a generalized motion of continuum media including solid skeleton, where $\boldsymbol{v} \equiv 0$[1]:

$$(2) \qquad\qquad \frac{\partial \varrho}{\partial t} + \nabla \cdot (\varrho \, \boldsymbol{v}) = 0.$$

Equation (2) is treated in the sense of distributions, that is as an integral identity

$$\int_{\Omega_T} \varrho \left(\frac{\partial \varphi}{\partial t} + \boldsymbol{v} \cdot \nabla \varphi \right) dx dt = 0$$

for the density

$$\varrho(\boldsymbol{x}, t) = \chi(\boldsymbol{x}, t)\varrho_f + \big(1 - \chi(\boldsymbol{x}, t)\big)\varrho_s,$$

which holds for any smooth probe function $\varphi(\boldsymbol{x}, t)$, vanishing at S^+, S^-, $t = 0$ and $t = T$.

In particular it follows the boundary condition [15]:

$$(v_n - V_n)\varrho_f = -V_n\varrho_s, \ \ \boldsymbol{x} \in \Gamma(t), \ \ t > 0,$$

or

$$(3) \qquad v_n = -V_n\frac{(\varrho_s - \varrho_f)}{\varrho_f} \iff V_n - v_n = \frac{\varrho_s}{\varrho_f}V_n, \ \ \boldsymbol{x} \in \Gamma(t), \ \ t > 0,$$

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[1]The skeleton is immobile!

where V_n is the velocity of the free boundary S and v_n is the normal velocity of the fluid at this boundary. Finally, the continuity equation in its differential form in the pore space $\Omega_f(t)$ for $t > 0$ is written as

$$(4) \qquad \nabla \cdot \boldsymbol{v} = 0.$$

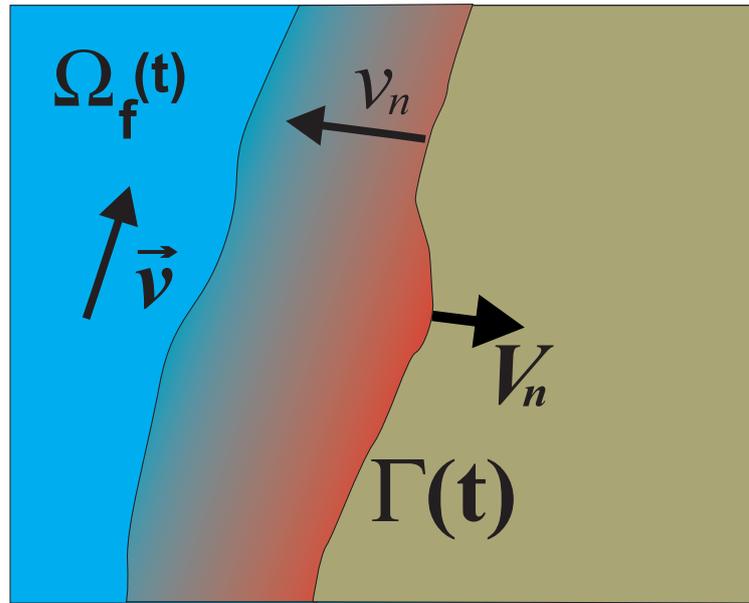The concentration c of the reagent satisfies to the diffusion-convection equation

FIG. 2. Diffusion and convection near the free boundary

$$(5) \qquad \frac{\partial c}{\partial t} + \boldsymbol{v} \cdot \nabla c = \alpha_c \triangle c,$$

and concentrations c_1, c_2,..., c_n of products of chemical reactions in $\Omega_f(t)$ — to the transport equations

$$(6) \qquad \frac{\partial c_i}{\partial t} + \boldsymbol{v} \cdot \nabla c_i = 0, \ \ i = 1, ..., n.$$

In $(1) - (6)$

$$\alpha_\mu = \frac{\mu}{T \, Lg \, \rho^0}, \ \ \alpha_c = \frac{D \, T}{L^2}, \ \ p^* = \rho_f \frac{L^2}{T^2},$$

where μ is dynamical viscosity of the fluid within the pore space, $\chi(\boldsymbol{x}, t)$ is the indicator function of the pore space ($\chi = 1$ in $\Omega_f(t)$ and $\chi = 0$ in $\Omega_s(t)$), ϱ_s and ϱ_f are dimensionless densities of the solid skeleton and pore liquids correspondingly, correlated with the mean density of water ρ^0, L is a characteristic size of the domain in consideration, T is a characteristic time of the process, g is the gravity acceleration, ρ_c is a density of the active component and D is a diffusivity coefficient (see Fig. 2).

Now let us derive the basic boundary conditions for the concentrations c, c_1, c_2,..., c_n at the free boundary. First of all we obtain these conditions for one dimensional case, that is with single spatial variable. In this statement the pore

space is considered as $\Omega_f(t) = \{x : 0 < x < X(t)\}$ and $\Gamma(t) = \{x : x = X(t)\}$ be a free boundary (see Fig. 3). Then

$$\frac{\partial v}{\partial x} = 0, \ 0 < x < X(t),$$

(7)

$$\frac{\partial c}{\partial t} + v\frac{\partial c}{\partial x} = \alpha_c \frac{\partial^2 c}{\partial x^2}, \ 0 < x < X(t),$$

$$\alpha_c \frac{\partial c}{\partial x} - v(t)\, c = 0 \text{ at } x = 0,$$

$$\frac{\partial c_i}{\partial t} + v\frac{\partial c_i}{\partial x} = 0, \ 0 < x < X(t), \ c_i = 0 \text{ at } x = 0, \ i = 1, ..., n.$$

The total masses of the reagent and products of the reactions in $\Omega_f(t)$ are given by the integrals

(8) $$M(t) = \int_0^{X(t)} c(x,t)dx, \ M_i(t) = \int_0^{X(t)} c_i(x,t)dx, \ i = 1, ..., n.$$

The rate of change of these variables in time is computed as:

$$\frac{dM}{dt} = \frac{dX}{dt} c\big(X(t),t\big) + \int_0^{X(t)} = \frac{\partial c}{\partial t}(x,t)dx$$

$$= \frac{dX}{dt} c\big(X(t),t\big) + \int_0^{X(t)} \frac{\partial}{\partial x} \left(\alpha_c \frac{\partial c}{\partial x}(x,t) - v(t)\, c(x,t) \right) dx$$

$$= \left(\frac{dX}{dt}(t) - v(t) \right) c(X(t),t) + \alpha_c \frac{\partial c}{\partial x}(X(t),t),$$

$$\frac{dM_i}{dt} = \frac{dX}{dt} c_i\big(X(t),t\big) + \int_0^{X(t)} \frac{\partial c_i}{\partial t}(x,t)dx$$

$$= \frac{dX}{dt} c_i\big(X(t),t\big) - \int_0^{X(t)} v(t)\frac{\partial c_i}{\partial x}(x,t)dx$$

$$= \left(\frac{dX}{dt}(t) - v(t) \right) c_i(X(t),t) = \frac{\varrho_s}{\varrho_f}\frac{dX}{dt} c_i(X(t),t), \quad i = 1, ..., n.$$

Straightforward calculations of these integrals with the use of (3) and (7) at $x = 0$, gives:

$$\frac{dM}{dt} = (\frac{dX}{dt} - v)c + \alpha_c \frac{\partial c}{\partial x},$$

(9)

$$\frac{dM_i}{dt} = \frac{\varrho_s}{\varrho_f}\frac{dX}{dt} c_i, \ i = 1, ..., n, \text{ at } x = X(t).$$

Last relations mean that the change of concentrations of products of chemical reactions occurs only at $\Gamma(t)$. The values $\dfrac{dM}{dt}, \ \dfrac{dM_i}{dt}, \ i = 1, \ldots, n$, are called **rates**

of chemical reactions and are defined from the complimentary laws of chemical kinetics:

$$(10) \qquad \frac{dM}{dt} = -\beta\,\varphi(c), \quad \frac{dM_i}{dt} = \beta\,\bar\varphi_i(c), \; i = 1,...,n,$$

where $\varphi(c)$, $\bar\varphi_i(c)$, $i = 1,...,n$ are given positive functions.

On the other hand, the mass conservation implies

$$(11) \qquad \varrho_s\frac{dX}{dt} - \varrho_f\frac{dM}{dt} = \sum_{i=1}^{n}\varrho_i\frac{dM_i}{dt},$$

where ϱ_c, $\varrho_1, ..., \varrho_n$ are dimensionless densities of reagent and products of chemical reactions.

Relations (9)–(11) result

$$(12) \qquad \frac{dX}{dt}(t) = \beta\,\varphi_0\left(c\left(X(t),t\right)\right), \; c_i(X(t),t) = \varphi_i\Big(c\big(X(t),t\big)\Big), \; i = 1,...,n,$$

and

$$(13) \qquad \left(\frac{dX}{dt}(t) - v(t)\right)c(X(t),t) + \alpha_c\frac{\partial c}{\partial x}(X(t),t) = -\beta\,\varphi\Big(c\big(X(t),t\big)\Big),$$

where

$$\varrho_s\varphi_0 + \varrho_c\varphi = \sum_{i=1}^{n}\varrho_i\bar\varphi_i, \;\; \varphi_i = \frac{\varrho_s}{\varrho_f}\frac{\bar\varphi_i}{\varphi_0}, \; i = 1,\ldots,n.$$

Coming back to (4) – (6) we conclude that in a general case mass conservation laws for concentrations at the free boundary have a form

$$(14) \qquad (V_n - v_n)\,c + \beta\,\varphi(c) + \alpha_c\frac{\partial c}{\partial n} = 0, \; \boldsymbol{x} \in \Gamma(t),$$

$$(15) \qquad c_i = \varphi_i(c), \; i = 1,\ldots,n, \quad \boldsymbol{x} \in \Gamma(t),$$

$$(16) \qquad V_n = \beta\,\varphi_0(c), \; \boldsymbol{x} \in \Gamma(t),$$

where V_n is a normal velocity of $\Gamma(t)$ in the direction of the outward to $\Omega_f(t)$ normal $\boldsymbol{n}$, $v_n = \boldsymbol{v}\cdot\boldsymbol{n}$ is a normal liquid velocity, and $\frac{\partial c}{\partial n} = \nabla c\cdot\boldsymbol{n}$ is a normal derivative of c at $\Gamma(t)$.

It remains to supplement differential equations by missing boundary and initial conditions.

At the free boundary $\Gamma(t)$ the tangent velocity of the pore liquid vanishes:

$$(17) \qquad \boldsymbol{v} - \boldsymbol{v}\cdot\boldsymbol{n} = 0.$$

At the boundaries S^+ and S^-, which give injection and production wells, we put the normal tension in the liquid

$$(18) \qquad \left(\alpha_\mu\,\mathbb{D}(\boldsymbol{v}) - p\,\mathbb{I}\right)\cdot\boldsymbol{n} = -p^\pm(\boldsymbol{x},t)\boldsymbol{n},$$

where $\mathbb{I}$ is the unit matrix and

$$\mathbb{D}(\boldsymbol{v}) = \frac{1}{2}(\nabla\boldsymbol{v} + \nabla\boldsymbol{v}^*).$$

At the injection wells S^+ we put concentrations of the reagent and products of chemical reactions

$$(19) \qquad c_i = 0, \; i = 1,\ldots,n, \quad c = c^+(\boldsymbol{x},t).$$

At the production wells

(20) $$\nabla c \cdot \boldsymbol{n} = 0.$$

On the impermeable boundary S^0

(21) $$\boldsymbol{v} = 0, \quad \nabla c \cdot \boldsymbol{n} = 0.$$

The problem is ended with initial conditions

(22) $$\Gamma(0) = \Gamma_0, \ c(\boldsymbol{x}, 0) = c_0(\boldsymbol{x}), \ c_i(\boldsymbol{x}, 0) = 0, \ i = 1, ..., n, \ \boldsymbol{x} \in \Omega_0.$$

The system of differential equations (1), (4), (5), (6), completed with boundary and initial conditions (3), (14) – (22) forms desired mathematical model describing leaching at the microscopic level.

Note that the problem (1), (3)-(5), (14), (16)–(18), (20)-(22) for the liquid velocity and pressure, concentration of the active admixture, and the free boundary is independent of the problem (6), (15), (19), (22) for concentrations of products of chemical reactions.

2.2. One dimensional microscopic model: numerical implementations. Here we consider the simplest 1D geometry, when there are fluxes along x-axis only and the free boundary is just a moving point $x = X(t)$ as it is presented in Figure3.
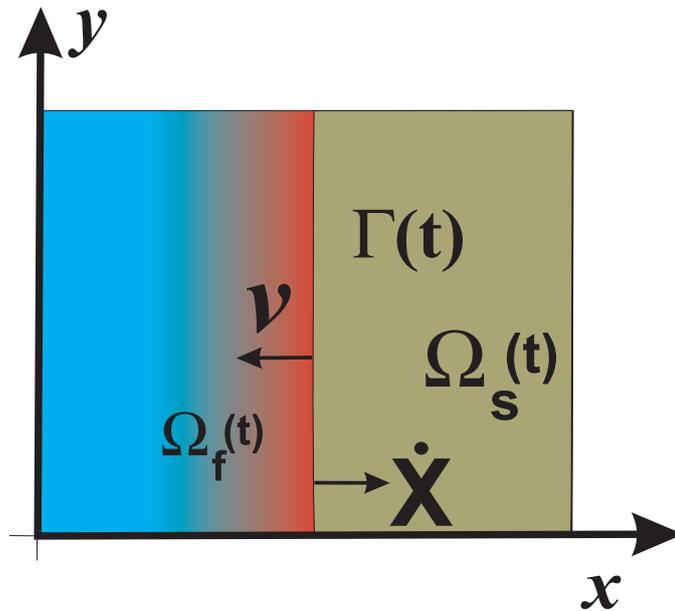

FIG. 3. One dimensional structure

For one spatial variable the differential equations (1) – (3), (22) in the domain $0 < x < X(t)$ for $t > 0$ are rewritten as follows:

(23) $$\frac{\partial p}{\partial x} = 0,$$

(24) $$\frac{\partial v}{\partial x} = 0,$$

$$(25) \qquad \frac{\partial c}{\partial t} + v\frac{\partial c}{\partial x} = \alpha_c \frac{\partial^2 c}{\partial x^2},$$

$$(26) \qquad \frac{\partial c_i}{\partial t} + v\frac{\partial c_i}{\partial x} = 0, \ \ i = 1, ..., n.$$

Boundary and initial conditions (14) – (22) are transformed to

$$(27) \qquad p(0,t) = p^+(t), \ \ c(0,t) = c^+(t), \ \ t > 0,$$

$$(28) \qquad \frac{dX}{dt} = \beta\,\varphi_0(c), \ \ x = X(t), \ \ t > 0,$$

$$(29) \qquad \Big(\frac{dX}{dt} - v\Big)c + \beta\,\varphi(c) + \alpha_c\frac{\partial c}{\partial x} = 0, \ \ x = X(t), \ t > 0,$$

$$(30) \qquad c_i(X(t),t) = \varphi_i(c), \ \ i = 1, ..., n, \ \ x = X(t), \ \ t > 0,$$

$$(31) \qquad v\,(t) = -\frac{dX}{dt}(t)\frac{(\rho_s - \rho_f)}{\rho_f}, \ \ t > 0,$$

$$(32) \qquad X(0) = X_0, \ \ c(x,0) = c_0(x), \ \ 0 < x < X_0.$$

Let us consider some particular behavior of chemical reaction:

$$(33) \qquad \varphi(c) = c^\nu, \ \ \bar\varphi_i(c) = \beta_i\,c^{\nu_0}$$

where $\nu_1 = \nu - \nu_0 > 0$. It follows

$$(34) \qquad \varphi_0(c) = \delta_0 c^{\nu_0}(1 - \delta_1\,c^{\nu_1}), \ \ \varphi_i(c) = \frac{\gamma_i}{(1 - \delta_1\,c^{\nu_1})},$$

where

$$\delta_0 = \sum_{i=1}^{n}\frac{\varrho_i}{\varrho_s}\beta_i, \ \ \delta_1 = \frac{\varrho_c}{\varrho_s\,\delta_0} < 1.$$

Let us fix now the characteristic length $L = 40$ μm, time $T = 1$ sec, $\delta_0 = 1$, $\delta_1 = 0,5$, $\gamma_1 = 0,01$, $\nu_1 = 0,2$ and suppose that the product of the chemical reaction is the single substance, that is $n = 1$. Now let us analyze how does the concentration of the product of chemical reaction at free boundary changes for different β, ν_0 and c^+.

(1) Let us start with parameter β in equation (28). This parameter governs the rate of the chemical reaction which is proportional to the velocity of the free boundary $x = X(t)$. The result is presented in Fig.4. As one can see the concentration decreases when the β increases. Really, when β increases the free interface moves faster, the volume of the target area id increased, hence concentration of the active reagent is decreased. This follows decreasing of the rate of chemical processes and finally diminishing of the concentration of the product of a chemical reaction. Let us pay attention to the decrease of the concentration of the product with time increase. It has the same nature as its decrease with β increase — the moving of the free surface is so fast, that diffusion of the reagent does not compensate its consumption in the reaction. Hence, the concentration of the reagent is decreased and, hence, the amount of the product is decreased too.
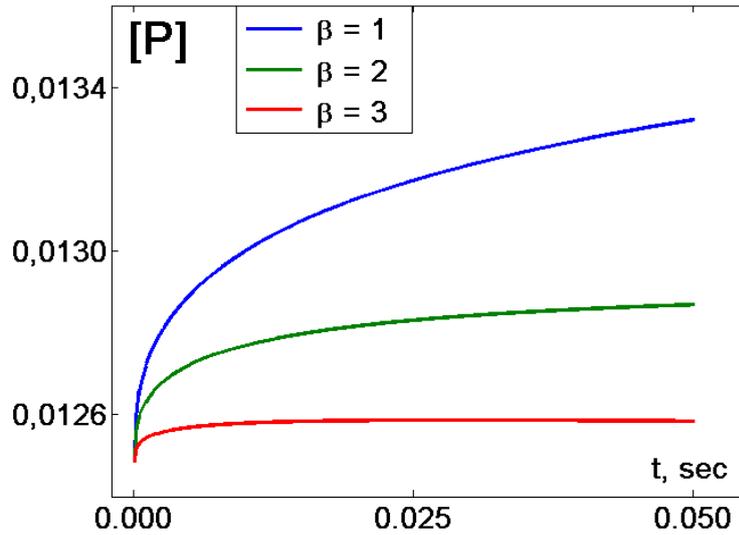
FIG. 4. Concentration of product of chemical reaction at the free boundary for different β

(2) The curve plotted in Fig.5 represents the impact of the concentration of the injected reagent to the concentration of the product. The answer is the absolutely expectable: there is direct proportion — the higher is the concentration of the injected reagent the higher is is the concentration of the product.

(3) Finally let us consider the concentration of the product of a chemical reaction in dependence of parameter $\nu_0 \geq 1$ (see 33). This parameter governs the rate of the chemical reaction in the part of the quantity of the products of interactions of the reagent and the skeleton: the higher is ν_0 the faster is increased amount of the product of the reaction. Therefore the amount of the product is increased at the free boundary as well.

3. The macroscopic model

The system derived in the previous section describes exactly the leaching at the pore scale. But its application to analyze the processes for realistic scales is impossible and needs to be upscaled in the special manner. Really, the classical upscaling is not applicable just because of the extremely fast oscillations of characteristic function. Usually homogenization is based on the periodicity of function χ:

$$\chi = \chi(\frac{\boldsymbol{x}}{\varepsilon_0}),$$

where ε_0 is a dimensionless pore size and $\chi(\boldsymbol{y})$ is known 1 – periodic function. Now, one chooses

$$\chi = \chi^\varepsilon = \chi(\frac{\boldsymbol{x}}{\varepsilon}), \ \ 0 < \varepsilon < \varepsilon_0,$$
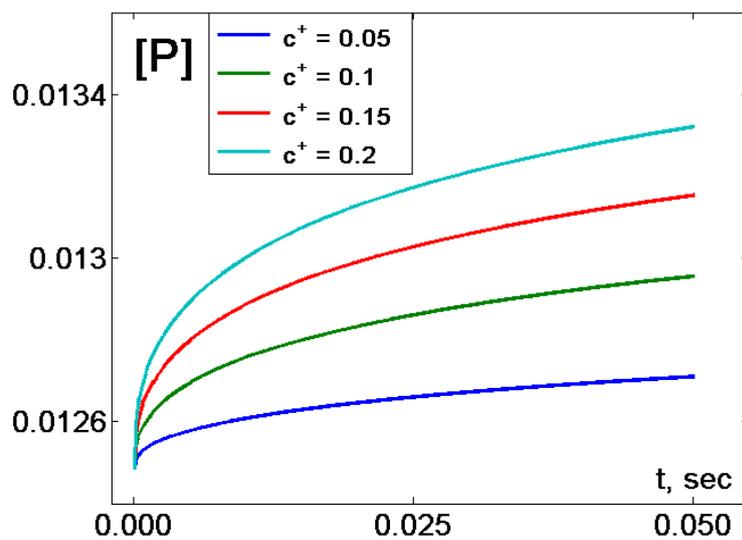
FIG. 5. Concentration of product of chemical reaction at the free boundary for different c^+
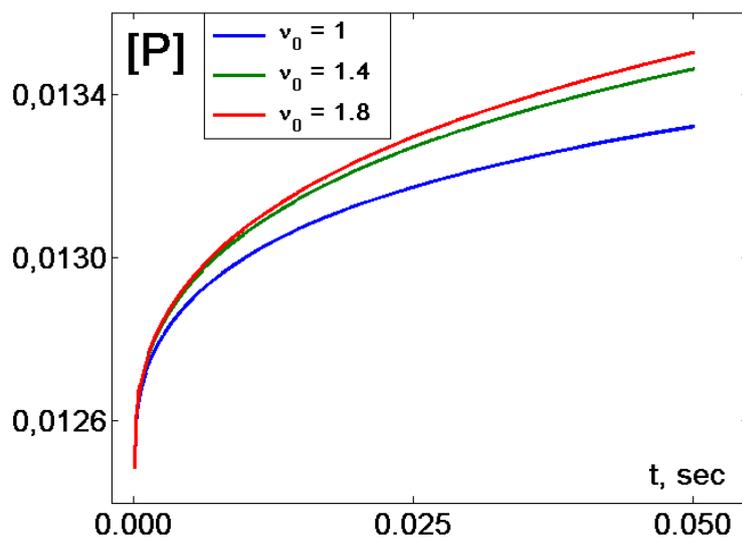

FIG. 6. Concentration of product of chemical reaction at the free boundary for different ν_0

and let ε goes to zero. The homogenization consists of finding the limit of corresponding to χ^ε solutions $\boldsymbol{v}^\varepsilon$, p^ε, c^ε, c_i^ε and the homogenized system for these limits. For sufficiently small ε_0 the solution to this homogenized system is closed to the solution for $\chi = \chi^{\varepsilon_0}$.

For our case the characteristic function of the pore space χ is variable in time and space and is given at $t = 0$ only. To solve the problem we suppose that

$$\chi = \chi^\varepsilon = \chi(\boldsymbol{x}, t, \frac{\boldsymbol{x}}{\varepsilon}) + o(\varepsilon), \ \ 0 < \varepsilon < \varepsilon_0,$$

where $\chi(\boldsymbol{x}, t, \boldsymbol{y})$ is 1-periodic in $\boldsymbol{y}$ function, and construct the upscaled system of equations as $\varepsilon \to 0$. Mathematically implementation of this approach is too complicated due to nonlinearity of the problem and necessity to search for unknown characteristic function χ^ε. Therefore at the moment we choose to be restricted with formal, but still physically justified, easier version of upscaling (homogenization) which is based on the representations:

$$\beta = \lambda\varepsilon, \ \alpha_\mu = \mu_1\varepsilon^2, \ \alpha_c = D_0,$$

$$\boldsymbol{v}^\varepsilon(\boldsymbol{x}, t) = \boldsymbol{V}(\boldsymbol{x}, t, \frac{\boldsymbol{x}}{\varepsilon}) + o(\varepsilon),$$

$$p^\varepsilon(\boldsymbol{x}, t) = p(\boldsymbol{x}, t) + o(\varepsilon),$$

$$c^\varepsilon(\boldsymbol{x}, t) = c(\boldsymbol{x}, t) + o(\varepsilon), \ \nabla c^\varepsilon(\boldsymbol{x}, t) = \nabla c(\boldsymbol{x}, t) + \nabla_y C(\boldsymbol{x}, t, \frac{\boldsymbol{x}}{\varepsilon}) + o(\varepsilon),$$

$$c_i^\varepsilon(\boldsymbol{x}, t) = c_i(\boldsymbol{x}, t) + o(\varepsilon), \quad i = 1, \ldots, n$$

with 1-periodic in $\boldsymbol{y}$ functions $\boldsymbol{V}(\boldsymbol{x}, t, \boldsymbol{y})$ and $C(\boldsymbol{x}, t, \boldsymbol{y})$.

Using these representations and well – known mathematical formula

$$\lim_{\varepsilon \to 0} \int_Q U(\boldsymbol{x}, t, \frac{\boldsymbol{x}}{\varepsilon}) dx = \int_Q \Big(\int_Y U(\boldsymbol{x}, t, \boldsymbol{y}) dy \Big) dx$$

for 1-periodic in $\boldsymbol{y} \in Y$ function $U(\boldsymbol{x}, t, \boldsymbol{y})$, we find homogenized system for functions $\boldsymbol{v}(\boldsymbol{x}, t) = \int_Y \boldsymbol{V}(\boldsymbol{x}, t, \boldsymbol{y}) dy$, $p(\boldsymbol{x}, t)$, and $c(\boldsymbol{x}, t)$ with unknown coefficients.

More precisely, this system consists of dynamic equations

$$(35) \qquad \boldsymbol{v} = -\frac{1}{\mu_1}\mathbb{A} \cdot \nabla p,$$

$$(36) \qquad \nabla \cdot \boldsymbol{v} = \frac{(\varrho_s - \varrho_f)}{\varrho_f}\frac{\partial m}{\partial t}$$

for the velocity $\boldsymbol{v}$ and pressure p of pore liquid, and the diffusion – convection equation

$$(37) \qquad m\frac{\partial \Phi(c)}{\partial t} + \boldsymbol{v} \cdot \nabla c - D_0 \nabla \cdot (\mathbb{C} \cdot \nabla c) = -\Big(\frac{\varrho_s}{\varrho_f}c + \frac{\varphi(c)}{\varphi_0(c)} \Big)\frac{\partial m}{\partial t}$$

for concentration c of the reagent. Here $\Phi(c) = c + \dfrac{\varphi(c)}{\varphi_0(c)}$ and unknown functions m (porosity of a medium) is given as:

$$m(\boldsymbol{x}, t) = \int_Y \chi(\boldsymbol{x}, t, \boldsymbol{y}) dy.$$

Matrices $\mathbb{A}$ and $\mathbb{C}$ are defined by a given microstructure. In particular:

$$\mathbb{C}(\boldsymbol{x},t) = \Big(m(\boldsymbol{x},t)\,\mathbb{I} + \int_Y \chi(\boldsymbol{x},t,\boldsymbol{y}) \big(\sum_{i=1}^{3} \nabla_y Q^{(i)}(\boldsymbol{x},t,\boldsymbol{y}) \otimes \boldsymbol{e}_i \big) dy \Big),$$

with unit matrix $\mathbb{I}$ and the standard cartesian basis $(\boldsymbol{e}_1, \boldsymbol{e}_2, \boldsymbol{e}_3)$. The product $\mathbb{B} = \boldsymbol{a} \otimes \boldsymbol{b}$ is defined as $\mathbb{B} \cdot \boldsymbol{c} = \boldsymbol{a}(\boldsymbol{b} \cdot \boldsymbol{c})$. The 1 – periodic in $\boldsymbol{y}$ functions $Q^{(i)}(\boldsymbol{x},t,\boldsymbol{y})$, $i = 1, 2, 3$ in each point $\boldsymbol{x} \in \Omega$ for $t > 0$ are solutions to the following periodic boundary problem

(38) $$\triangle_y Q^{(i)} = 0, \;\; \boldsymbol{y} \in Y_f(\boldsymbol{x},t),$$

(39) $$(\boldsymbol{e}_i + \nabla_y Q^{(i)}) \cdot \boldsymbol{\nu} = 0, \;\; \boldsymbol{y} \in \gamma(\boldsymbol{x},t) = \partial Y_f(\boldsymbol{x},t)$$

in the unknown subdomain $Y_f(\boldsymbol{x},t) \subset Y$ of the unit cube Y. In (39) $\boldsymbol{\nu}$ is the unit normal vector to the boundary $\gamma(\boldsymbol{x},t)$.

By analogy with the microscopic model, the behavior of the free boundary $\gamma(\boldsymbol{x},t)$ is governed by differential equation

(40) $$\frac{\partial}{\partial t}\chi(\boldsymbol{x},\boldsymbol{y},t) = \lambda\,\varphi_0\big(c(\boldsymbol{x},t)\big)\,|\nabla_y\,\chi(\boldsymbol{x},\boldsymbol{y},t)|$$

for the characteristic function $\chi(\boldsymbol{x},\boldsymbol{y},t)$ of the unknown domain $Y_f(\boldsymbol{x},t)$.

Finally, concentrations c_i, $i = 1, ..., n$ of the products of chemical reactions are solutions to the non-homogeneous transport equations

(41) $$m\,\frac{\partial c_i}{\partial t} + \boldsymbol{v} \cdot \nabla c_i = \frac{\rho_s}{\rho_f}\big(\varphi_i(c) - c_i\big)\frac{\partial m}{\partial t}.$$

The problem is ended with following boundary and initial conditions:

(42) $$p = p^{\pm}(\boldsymbol{x},t), \;\; \boldsymbol{x} \in S^{\pm}, \;\; t > 0,$$

(43) $$c_i = 0, \;\; i = 1, ..., n, \;\; c = c^+(\boldsymbol{x},t), \;\; \boldsymbol{x} \in S^+,$$

(44) $$\nabla c \cdot \boldsymbol{n} = 0, \;\; \boldsymbol{x} \in S^-, \;\; t > 0,$$

(45) $$\nabla c \cdot \boldsymbol{n} = 0, \;\; \boldsymbol{v} \cdot \boldsymbol{n} = 0, \;\; \boldsymbol{x} \in S^0, \;\; t > 0,$$

(46) $$c(\boldsymbol{x},0) = c_0(\boldsymbol{x}), \;\; c_i(\boldsymbol{x},0) = 0, \;\; i = 1, ..., n, \;\; \gamma(\boldsymbol{x},0) = \gamma_0(\boldsymbol{x}) \;\; \boldsymbol{x} \in \Omega.$$

One may see that the structure of the homogenized system and all its coefficients are well defined from the clear physical postulates and microstructure.

4. Two dimensional macroscopic model: numerical implementations

Numerical experiments presented below are performed to analyze how different parameters of the macroscopic model influence the specific features of the leaching process.

Let us start with description of geometrical and physical parameters of the statement.

(1) The target domain is unit square in dimensionless coordinates:

$$\Omega = \{-1 < x_1 < 1, \; -1 < x_2 < 1\}$$

with injection-producing boundaries

$$S^{\pm} = \{x_1 = \mp 1\}$$

and fixed interfaces

$$S^0 = \{x_2 = -1\} \cup \{x_2 = 1\}$$

(2) Our assumptions (34) about φ_0 and φ_1 (let us remind that at the moment we deal with chemical reaction producing the single component!) gives

$$\Phi = c + \frac{c^{\nu_1}}{\delta_0(1 - \delta_1 \, c^{\nu_1})}$$

;

(3) Other parameters are taken as $\delta_0 = 1$, $\delta_1 = 0,5$, $\nu = 2$, $\nu_1 = 1$, $p^* \cdot p^+ = 10$, $T = 3 \cdot 10^7$, $L = 40m.$, $D = 10^{-9}\frac{m^2}{sec}$, $p^- = 0$, $c_0 = 0.5$.

For this choice of parameters we performed the simulation of the concentration of a product of the chemical reaction at the production well for different values of:

- Concentration of the reagent at the injection well c^+ (see Fig.7);
- Parameter $\beta = \lambda \varepsilon$ which governs the intensity of a chemical reaction at the free surface (see Fig.8).
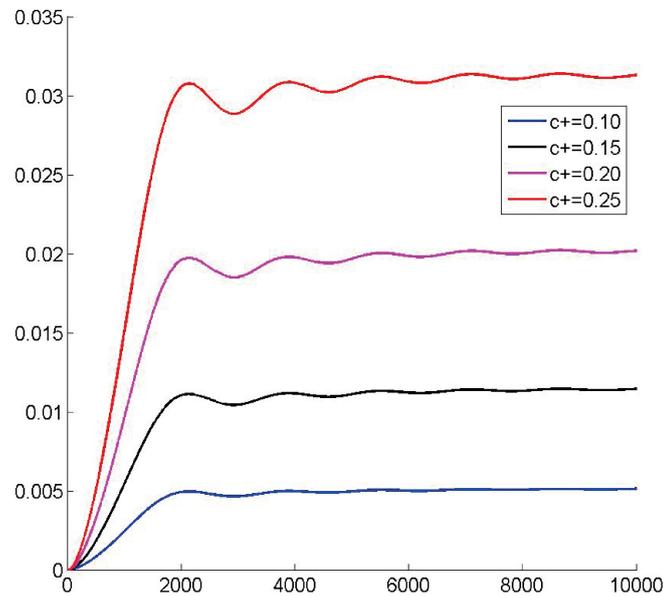

FIG. 7. The macroscopic model: concentration of product of chemical reaction at the production well for different concentration of the injected reagent c^+
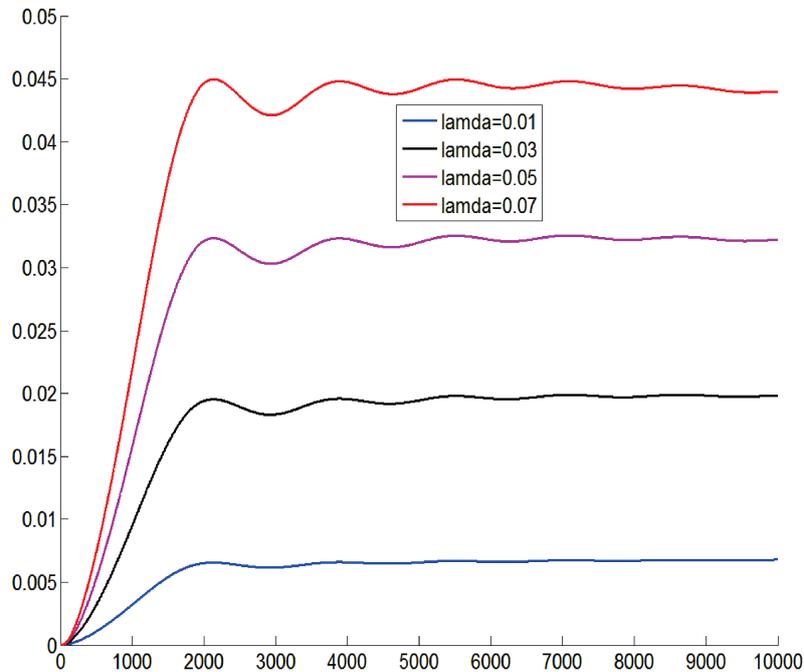
FIG. 8. The macroscopic model: concentration of product of chemical reaction at the production well for different λ

5. CONCLUSIONS

The new mathematical model, which describe the leaching process by interaction of an acid in pore liquid with the rock matrix. This approach is based on the detailed consideration of fundamental laws of mechanics and chemistry at the pore scale. It is clear that the obtained mathematical model cannot be used in practical applications, but its simple and mathematically correct form allows the further approximation in the system of homogenized equations. Some numerical implementations show the distinctive features of the model. For example, at the microscopic level to increasing values of the constant β in the rates of chemical reactions correspond decreasing values of concentrations of the reagent and products of chemical reactions at the free boundary (see Fig. 4-6). This is quite strange for chemists. But in the macroscopic model one has the usual situation: to increasing values of the constant $\beta = \lambda \varepsilon$ in the rates of chemical reactions correspond increasing values of the concentrations of products of chemical reactions at the productive wells (see Fig. 8). On the other hand, to to increasing values of input concentration

c^+ always correspond increasing values of the concentrations of products of chemical reactions at the free boundary in the microscopic model (see Fig. 4-6), and increasing values of the concentrations of products of chemical reactions at the productive wells (see Fig. 7).

Note also, that in the introduction we discussed the possibility of oscillations for the microscopic model. Unfortunately we cannot find these oscillations in our numerical implementations for the microscopic model maybe because they are too small and to see them one needs to perform computations with much more precision. But at the macroscale these oscillations are evident and in the nearest future we plan to perform a special series of numerical experiments to understand the process in the greater details.

References

[1] F. Golfier, C. Zarcone, B. Bazin, R. Lenormand, D. Lasseux and M. Quintard, *On the ability of a Darcy-scale model to capture wormhole formation during the dissolution of a porous medium*, J. Fluid Mech., **457** (2002), 213–254. Zbl 1016.76079

[2] Kalia Nitika, Balakotaiah Vemuri, *Effect of medium heterogeneities on reactive dissolution of carbonates*, Chemical Engineering Science, **64** (2009), 376–390.

[3] C.E. Cohen, D. Ding, M. Quintard, B. Bazin, *From pore scale to wellbore scale: Impact of geometry on wormhole growth in carbonate acidization*, Chemical Engineering Science, **63** (2008), 3088 – 3099.

[4] M.K.R. Panga, M. Ziauddin, V. Balakotaiah, *Two-scale continuum model for simulation of wormholes incarbonate acidization*, A.I.Ch.E.Journal, **51** (2005), 3231–3248.

[5] R. Burridge and J. B. Keller, *Poroelasticity equations derived from microstructure*, Journal of Acoustic Society of America **70**:4 (1981), 1140–1146. Zbl 0519.73038

[6] E. Sanchez-Palencia, *Non-Homogeneous Media and Vibration Theory*, Lecture Notes in Physics, **129**, Springer-Verlag, New York, 1980. MR0578345

[7] D. Lukkassen, G. Nguetseng, P. Wall, *Two-scale convergence*, Int. J. Pure and Appl. Math. **2**:1 (2002), 35–86. MR1912819

[8] A. Meirmanov, *Mathematical models for poroelastic flows*, Atlantis Press, Paris, 2013.

[9] A. Meirmanov, *Nguetseng's two-scale convergence method for filtration and seismic acoustic problems in elastic porous media*, Siberian Mathematical Journal, **48**:3 (2007), 519–538. MR2347913

[10] A. Meirmanov, *A description of seismic acoustic wave propagation in porous media via homogenization*, SIAM J. Math. Anal., **40**:3 (2008), 1272–1289. MR2452887

[11] A. Meirmanov, *Double porosity models in incompressible poroelastic media*, Mathematical Models and Methods in Applied Sciences, **20**:4 (2010), 635–659.

[12] A. Meirmanov, *The Muskat problem for a viscoelastic filtration, Interfaces and Free Boundaries*, **13**:4 (2011), 463–484.

[13] A. Meirmanov, *The Stefan Problem*, Walter de Gruyter, Berlin-New York, 1992. MR1154310

[14] L.E. Malvern, *Introduction to Mechanics of a Continuum Medium*, Prentice–Hall, Inc. Englewood Cliffs, N.J., 1969.

[15] G.B. Whitham, *Linear and nonlinear waves*, Willey, ISBN 978-0-471-94090-6 (1999). MR1699025

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